Molecular Modeling of Mechanical Properties of Amorphous Atactic Poly(propylene oxide)

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1. Introduction

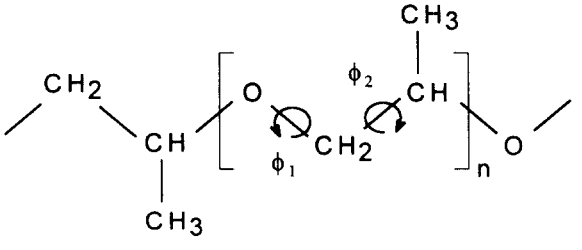
In general, the macroscopic properties of polymers are based on their microscopic structures. Since the mechanical properties are important in a practical viewpoint. Computer simulation, i.e., molecular dynamics and molecular mechanics, has played an important role to understand and characterize the mechanisms of mechanical behavior.

Suter and co-workers have studied the elastic and plastic response of glassy polymers, and calculated some mechanical constants[1-3]. Clarke and Brown have constructed the amorphous dense system of polyethylene-like polymer by the NPT molecular dynamics and simulated its deformation under external tension condition[4]. Fan and Hsu have studied mechanical properties of various polymer systems and obtained the results comparable with the real material[5-8]. The concepts and procedures chosen in molecular modeling have been justified, so that the simulations could treat the model more precisely.

In this study, the mechanical behavior of amorphous atactic poly(propylene oxide)(PPO) under uniaxial tensile condition was examined and the elastic constants were calculated. Also, the conformational changes of PPO were investigated under deformation.

2. Model and Simulation

The full atomic model contained one PPO chain(DP=90) with 902 atoms as follows:



The bulk amorphous state was simulated by use of periodic boundary conditions. A polymer chain was packed into a triclinic cell, and the cell was infinitely repeated in a three-dimensional space. The amorphous cell constructed was equilibrated using both energy minimization and molecular dynamics. The cell density was optimized during

equilibration. To avoid the local energy minimum state, NVT simulation was carried out at 1000K and 298K, and then NPT simulation was done to approach the stress-free isotropic state. PPO cells were extented and relaxed by energy minimization repeatedly until the target extension was obtained. During the procedure, the internal stresses were monitored and used to plot the stress-strain curve. Five samples were prepared and their mechanical properties were averaged.

3. Results and Discussion

Using radial distribution function g(r) it should be verified whether the cell was really amorphous. Function g(r) is defined as the probability of finding any two atoms at a distance r apart in the simulated structure relative to the expected probability calculated for a completely homogeneous phase with random atoms[9]. The calculated radial distribution function for a simulated PPO sample is shown in Fig.1. The value of g(r) in the range r>0.4 nm demonstrate the amorphous nature of the sample, i.e., complete absence of long-range order.

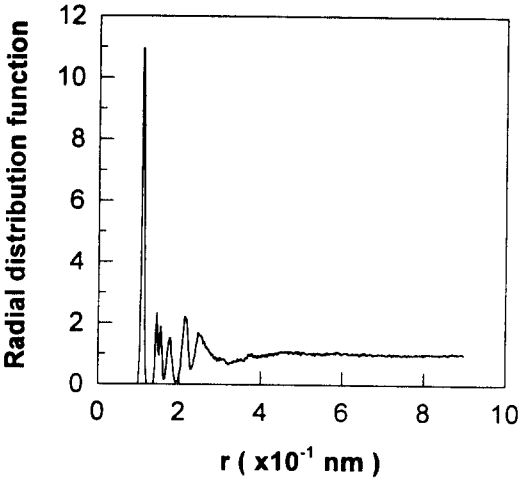


Fig.1. Radial distribution function for an amorphous PPO cell.

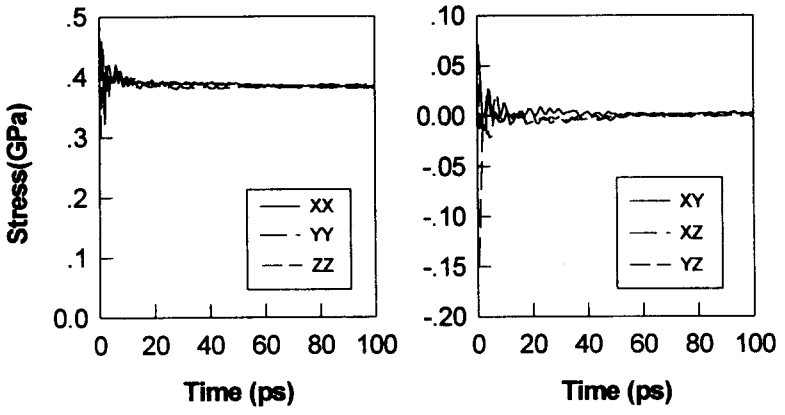


Fig.2. The change of stress components of an amorphous PPO cell in NPT molecular dynamics with time.

The stress state for a PPO sample is shown in Fig.2. The tensile and shear stress fall out to the same value. Therefore, we can accept this sample as a amorphous one in stress-free state

As shown in Fig.3, Stress-strain curves were obtained from these samples. In the case of sample shown in Fig.3, The density is ρ =0.9007 and Young's modulus is 59.96 GPa.

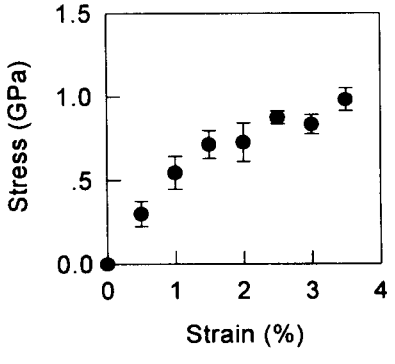


Fig.3. The stress-strain curve of an amorphous PPO cell.

Fig.4 Shows the torsional angle distribution before and after deformation(3.5%) of the sample. It was found that ϕ_1(CCOC) and ϕ_2(OCCO) did not experience drastic change.

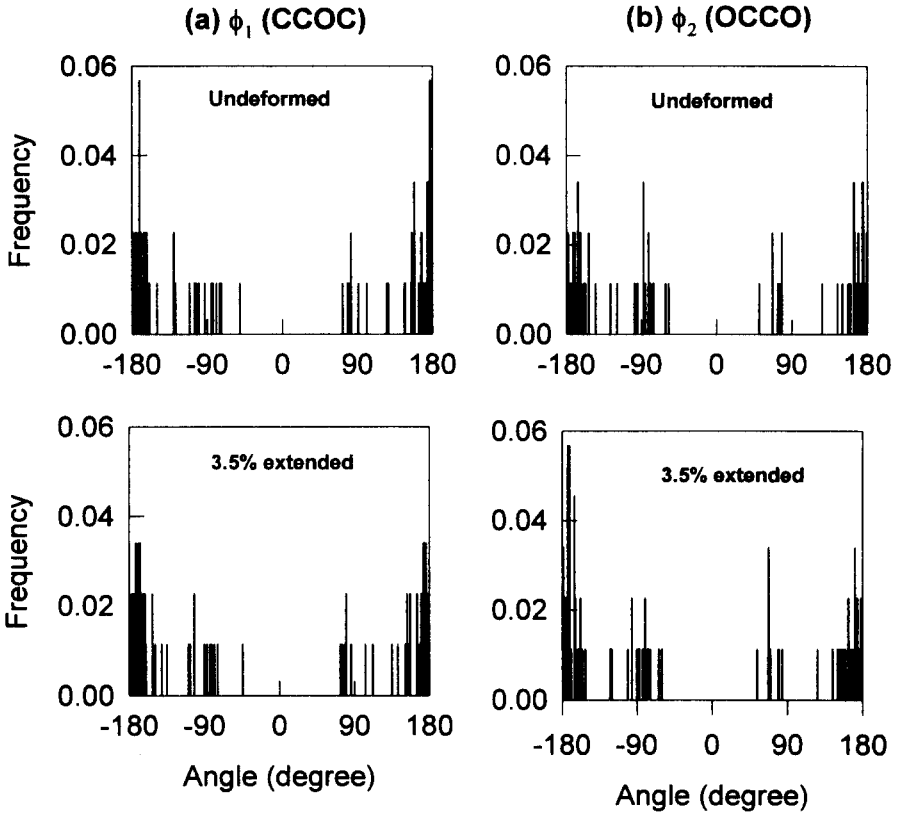


Fig.4. Torsional angle distribution of (a) ϕ_1(CCOC) and (b) ϕ_2(OCCO) in an amorphous PPO cell.

Conclusions

Using molecular mechanics and molecular dynamics, an amorphous atactic, stress-free poly(propylene oxide) model was prepared. This structure did not exhibit any evidence of long-range order in radial distribution function. The Young's modulus was calculated.

In elastic response of PPO, the significant change of conformation was not observed.

References

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